Synthesis and Structure of the Sulfur-Rich Macrocycle $(1,2\text{-}C_6H_4S_8)_2$[‡]

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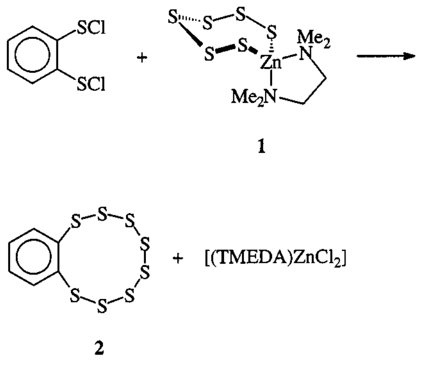
Benzenebis(sulfenyl chloride) and the zinc complex $(TMEDA)ZnS_6$ react at 25 °C to give the 20-membered heterocycle $(C_6H_4S_8)_2$ in addition to the monomer $1,2\text{-}C_6H_4S_8$.

Introduction

The transfer of polysulfido ligands S_n^{2-} from metal complexes to organic substrates has been extremely successful for the tailor-made synthesis of sulfur-rich diorgano polysulfanes $R{-}S_n{-}R$ ($n > 4$) which may be linear or cyclic.[1] Such compounds are often thermally unstable and subject to decomposition by nucleophilic attack, and therefore not easy to prepare by conventional synthetic methods such as those described in *Methodicum Chimicum*[2] and *Houben-Weyl*.[3] The most important metal polysulfido complexes used in this context are the titanocene derivatives $[(C_5H_5)_2TiS_5]$,[4-7] $[(C_5H_5)_2ClTi]_2S_3$ [8] and $[(C_5H_5)_2TiS_2]_2$ [6] as well as the zinc complex $[(TMEDA)ZnS_6]$ **1** (TMEDA: tetramethylethylenediamine).[9] These neutral complexes are soluble in organic solvents and react with organic sulfenyl chlorides almost quantitatively to give the corresponding polysulfanes containing between 5 and 11 cumulated sulfur atoms. For example, 1,2-benzenebis(sulfenyl chloride) reacts with **1** in carbon disulfide at ambient temperature to give the cyclic octasulfane $1,2\text{-}C_6H_4S_8$ **2** which was isolated in 60% yield (Scheme 1).[9]

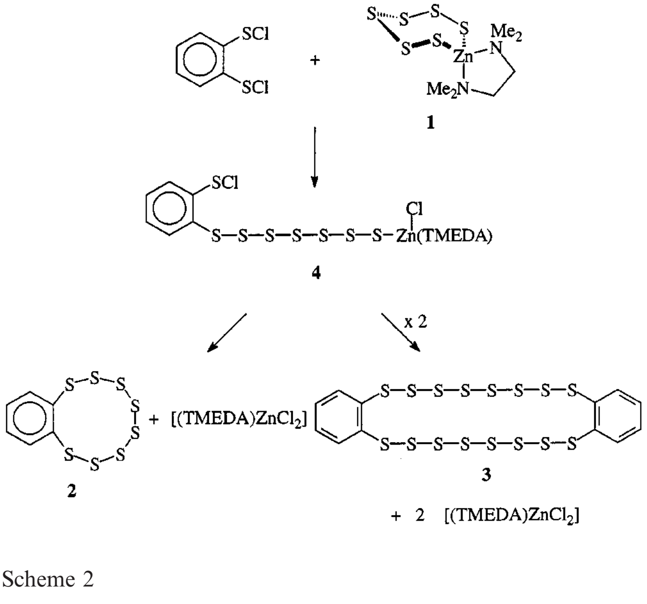


Scheme 1

Results and Discussion

On reinvestigating the reaction shown in Scheme 1 by reversed-phase HPLC analysis we observed that a second polysulfane is formed. This sulfane was isolated in 6% yield and characterized by single crystal X-ray crystallography as 5,6,7,8,9,10,11,12,17,18,19,20,21,22,23,24-hexadecathiadibenzo[*a*,*k*]cycloeicosene $(C_6H_4S_8)_2$ **3**. This macrocyclic product is obtained from carbon disulfide solutions as yellow crystals that contain one mol of CS_2 per mol of **3**. Recrystallization from dichloromethane resulted in pure **3**.

The formation of **3** can be understood by dimerization of the intermediate **4** resulting from the attack of the first sulfenyl group of $C_6H_4(SCl)_2$ on the zinc hexasulfido complex **1** (Scheme 2).



Scheme 2

The observation of **3** provides evidence that the reactive intermediate has a certain lifetime before it cyclizes *unimolecularly* to give **2**. It also follows from this mechanism that the formation of **3** will be promoted by higher concentrations of the reactants since **3** is the product of a *bimolecular* reaction. Consequently, the optimum experimental procedure for the preparation of **3** (see below) differs slightly from that of **2**.

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The laser Raman spectrum of **3**, excited at a wavelength of 1064 nm, exhibits a line at 1566 cm^{-1} for the asymmetric stretching mode of CS_2 as well as the characteristic lines of the aromatic rings at 3049, 1274, 1161, 1096 and 1039 cm^{-1}. The fourteen S−S stretching modes give rise to a very broad signal in the region 520−400 cm^{-1}, with a maximum at 467 cm^{-1}. Smaller peaks in this region can be observed at 502, 438 and 416 cm^{-1}.

The EI mass spectrum of **3** (sample temperature 227 °C) exhibits the typical fragments of a benzenepolysulfane although, as expected from the large molecular mass, no peak for the molecular ion was observed. Three types of ions were detected: S_n^+ ($n = 2-8$), RS_n^+ ($n = 1-3, 5$; $R = C_6H_4$) and $R_2S_n^+$ ($n = 2, 4, 6$); the base peak at $m/z = 140$ is assigned to $C_6H_4S_2^+$.

The ^{1}H NMR spectrum of **3** in CH_2Cl_2 is similar to, but not identical with, the spectrum of the monomer 1,2-$C_6H_4S_8$. It consists of two multiplets at $\delta = 7.41$ (4 H) and 7.83 (4 H) compared to $\delta = 7.43$ (2 H) and 7.74 (2 H) reported for the monomer.[9]

The identity and structure of compound **3** was established by a single crystal X-ray diffraction analysis carried out at 293 K. The centrosymmetric unit cell of the triclinic crystals contains one molecule of **3** together with two halves of a CS_2 molecule (see Figure 1). The macrocycle C_4S_{16} has the same ring size as *cyclo*-S_{20} [10] but a different conformation. The sulfur atoms form a kind of flat disc from which the aromatic rings are sticking out. These benzene rings are parallel to each other with S−C−C−S torsion angles of ±3.0(3)°. The S−S−S−S torsion angles are in the range 80.15(10)−108.95(5)° which is normal for cyclic polysulfanes. Their signs form the so-called *motif* of the sulfur chains and determine the conformation of the ring. If the torsion angles C−S−S−S and C−C−S−S are included the motifs of the two CCS_8CC segments are +++−+− − − − and − − − +−++++ (for the segment generated from the first one by inversion at the centre of symmetry). These motifs are different from those of all previous structurally characterized sulfur homocycles (S_n with $n = 6-14$, 18, 20).[11−13]

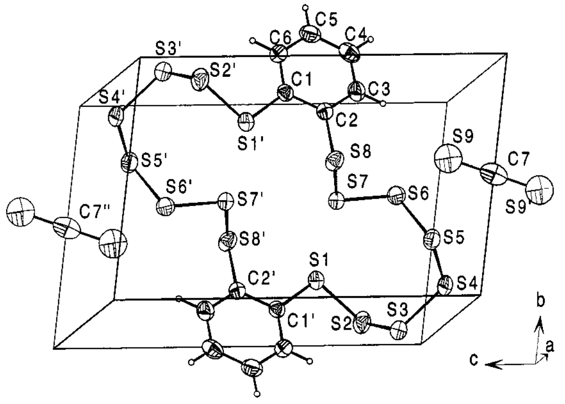

Figure 1. The centrosymmetric unit cell of $(C_6H_4S_8)_2 \cdot CS_2$ and numbering of atoms; selected internuclear distances [pm] and bond angles [°] as well as torsions angles [°]: C(1′)−(C(2′) 139.7(4), C(1′)−S(1) 178.5(3), S(1)−S(2) 202.99(11), S(2)−S(3) 206.32(13), S(3)−S(4) 205.41(12), S(4)−S(5) 204.65(11), S(5)−S(6) 205.72(12), S(6)−S(7) 204.83(11), S(7)−S(8) 205.86(11), S(8)−C(2) 178.1(3), C(7)−S(9) 153.7(2); C(2′)−C(1′)−S(1) 117.2(2), C(1′)−S(1)−S(2) 104.97(10), S(1)−S(2)−S(3) 108.35(5), S(2)−S(3)−S(4) 106.09(6), S(3)−S(4)−S(5) 108.22(5), S(4)−S(5)−S(6) 106.56(5), S(5)−S(6)−S(7) 106.40(4), S(6)−S(7)−S(8) 105.66(5), S(7)−S(8)−C(2) 102.09; C(2′)−C(1′)−S(1)−S(2) −165.1(2), C(1′)−S(1)−S(2)−S(3) −80.15(10), S(1)−S(2)−S(3)−S(4) −88.70(6), S(2)−S(3)−S(4)−S(5) 105.91(6), S(3)−S(4)−S(5)−S(6) −90.65(6), S(4)−S(5)−S(6)−S(7) 108.95(5), S(5)−S(6)−S(7)−S(8) 88.70(5), S(6)−S(7)−S(8)−C(2) 82.50(10), S(7)−S(8)−C(2)−C(1) −108.1(1)

The S−S bond lengths of **3** are in the narrow range of 203.0−206.3 pm. The arithmetic mean of 205.1 pm agrees well with the average bond length in orthorhombic α-S_8 (204.8 pm).[14]

To the best of our knowledge compound **3** is the most sulfur-rich heterocycle with more than 12 ring atoms that has ever been prepared as a pure material. This macrocycle may turn out to be a suitable ligand to coordinate transition metal ions. The discovery of **3** demonstrates that the ligand-transfer reactions to synthesize organic polysulfanes as mentioned in the Introduction are even more versatile than had been previously thought.

Experimental Section

General: Raman spectra were recorded with a Bruker RFS100 spectrometer at a sample temperature of 25 °C. Mass spectra were obtained with a AMS Intectra which is based on a Varian MAT 311A instrument. The ^{1}H NMR spectra were recorded with a Bruker ARX 200 spectrometer.

Preparation of 3: The synthesis was carried out under an atmosphere of dry dinitrogen and solvents were dried by conventional methods. A suspension of the zinc complex **1**[15] (326 mg, 0.94 mmol) in carbon disulfide (50 mL) was added within 1 hour to a solution of 1,2-benzenebis(sulfenyl chloride) (200 mg, 0.94 mmol) in dry carbon disulfide (20 mL). After stirring for 30 min. the precipitated $(TMEDA)ZnCl_2$ was filtered off, and the volume of the solution was reduced under vacuum to 15 mL. Methyl *tert*-butyl ether was then added until a slight turbidity appeared. Cooling of the mixture to −55 °C resulted in precipitation of more $(TMEDA)ZnCl_2$, which was filtered off. The solvent was completely evaporated under vacuum and the residue dissolved in the minimum volume of carbon disulfide (ca. 5 mL). After adding a few drops of cyclohexane the mixture was cooled to −55 °C whereupon $C_6H_4S_8$ precipitated and was filtered off. This procedure was repeated several times until all monomer was removed. On further addition of cyclohexane and cooling, the dimer **3** crystallized as single crystals. Yield: 19 mg **3**·CS_2 (6%). M.p. (dec.): ca. 96 °C. −Elemental analysis after recrystallization from dichloromethane: $C_{12}H_8S_{16}$ (665.2): calcd. C 21.67, H 1.21, S 77.12; found C 21.92, H 1.20, S 76.93.

Crystal Data for $(C_6H_4S_8)_2 \cdot CS_2$: $C_{13}H_8S_{18}$, $M = 741.28$, pale yellow crystal, crystal dimensions 0.42 × 0.32 × 0.28 mm, triclinic, space group $P\bar{1}$, $a = 7.45930(10)$ Å, $b = 8.1760(5)$ Å, $c = 11.6999(3)$ Å, $\alpha = 98.3690(10)°$, $\beta = 98.2780(10)°$, $\gamma = 94.4520(10)°$, $V = 695.04(3)$ Å^3, $Z = 1$, $D_c = 1.771$ Mg m^{-3}, $T = 293$ K, $R1 = 0.0462$, $wR2 = 0.1197$ for 4194 reflections with $I > 2\sigma(I)$ and 142 parameters. Data were collected with a Siemens Smart CCD diffractometer using Mo-K_α radiation ($\lambda = 0.71069$ Å). The structure was solved after Lorentz polarization and absorption correction (SAD-

ABS[16]) by direct methods (SHELXS[17]) and refined with anisotropic thermal parameters for the non-hydrogen atoms (SHELXL[18]). The hydrogen positions at the carbon atoms were refined with a riding model. The drawings were created with the DIAMOND[19] program.

Crystallographic data (excluding structure factors) for the structure included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-161467. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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